JRC Scientific and Technical Reports

Report on the $\delta_{VPDB}{}^{13}C$ measurements on Volatile Organic Compounds from groundwater samples using Compound Specific Isotope Analysis

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EUR 23689 EN - 2008

JRC EUROPEAN COMMISSION

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JRC 49545

EUR 23689 EN
ISBN 978-92-79-11164-8
ISSN 1018-5593
DOI 10.2787/17830

Luxembourg: Office for Official Publications of the European Communities

Printed in Belgium

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Abbreviations and acronyms

AMP/WP: Annual Management Plan/ Work Programme
BTEX: acronym for Benzene, Toluene, Ethylbenzene and Xylene isomers (i.e. *para*-, *meta*- and *ortho*-)
cDCE: *cis*-dichloroethene
tDCE: *trans*-dichloroethene
CSIA: Compound Specific Isotope Analysis
EA-IRMS: Elemental Analyser - Isotope Ratio Mass Spectrometry
FP7: Seventh Framework Programme
GC/C-IRMS: Gas Chromatography/ Combustion Isotope Ratio Mass Spectrometry
GC-MS: Gas Chromatography-Mass Spectrometry
GUMWB: GUM workbench
hSPME: headspace Solid Phase Microextraction
IRMS: Isotope Ratio Mass Spectrometry
PCE: tetrachloroethene
PDMS: polydimethylsiloxane
SPME: solid phase microextraction
TCE: trichloroethene
VOCs: Volatile Organic Compounds
VO-Cl: Volatile Organic – Chlorinated compounds

1. Introduction

The "VO-Cl pollution" project aims at applying Compound Specific Isotope Analysis (CSIA) methods for carbon - already developed at IRMM (Woulé Ebongué et al., 2009a, b) - targeting organic contaminants for source fingerprinting and apportionment. For this work, those methods are applied on Volatile Organic Chlorinated compounds from groundwater samples.
This project is a subproject of the institutional project "AMP/WP-FP7-22007-Source identification of BTEX and VO-Cl contamination in soil and water using isotopic methods". This work aims at supporting the European legislation such as the Directive 2006/12/EC specifically dedicated to VO-Cl pollution in groundwater. The Flemish Institute for Technological Research: VITO is the main customer and collaborator for this project.

The objectives of this project were to:
- allocate and fingerprint the carbon isotopic signatures of a selection of contaminants to their specific sources suspected of being responsible for the contaminant plume in the aquifer of the industrial site of Borsbeek (Belgium).
- assess the biodegradation extent in the investigated field using isotopic data.

This investigated industrial site is seated in Borsbeek which is located at about 10 km southeast of Antwerpen (Belgium). Former soil and groundwater investigations carried out by VITO indicated the presence of underground contamination by VO-Cl (Volatile organic chlorinated compounds) with PCE as main contaminant. Historical information linked this recorded contamination to the activities of two former dry cleaning facilities, in operation between 1971 and 2002 (dry cleaning 1) and between 1971 and 1974 (dry cleaning 2), respectively (Figure 1). Aromatic hydrocarbons: i.e. benzene, toluene, ethylbenzene, and xylene isomers, have been detected as well. The presence of those compounds can provide an evidence for an additional groundwater contamination due to gas work activities in or near this site.

In order to monitor the evolution of the $\delta_{PCE,\ VPDB}{}^{13}C$ of and that of its daughter products TCE and DCE, during reductive dechlorination in the investigated field, two duplicated sets of experimental batches, were investigated out at VITO, under controlled conditions similar to that of that field. Non-contaminated groundwater (further artificially contaminated by PCE) and the micro-organisms living in non-contaminated soil samples from the Borsbeek site were used for these experiments. The results from these experiments could help to evaluate the relative contribution of the microbial degradation in the changes of the carbon isotopic compositions of the contaminants observed in the field.

This report describes the work done at IRMM for this study: the material, the techniques and the methods used for measuring the $\delta_{VPDB}{}^{13}C$ of the VO-Cl in the 25 groundwater samples from the selected industrial site and 11 samples from experimental batches. This report also describes how the $\delta_{VPDB}{}^{13}C$ data with their combined uncertainties were calculated using GUMWB software.

2. Materials

2.1. Field samples

Twenty-five groundwater samples, selected along the contaminated plume in the aquifer of an industrial site located in Borsbeek (Belgium), were analysed at IRMM for their $\delta_{VPDB}{}^{13}C$.

These twenty-five groundwater samples were taken using a network of fifteen monitoring wells noted in Figure 1. The sampling was done in two successive campaigns.

- Fifteen groundwater samples were taken in January 2007, at different depths ranging from 3 to 13 meters below the ground surface, in the wells W1.1, 1.2, 2, 7, 10, 11, 12, 13, 14 and 15 (in blue in Figure 1).
- The second sampling campaign was performed later, in September 2007 where 11 samples were taken at smaller depths ranging from 3 to 6 meters below the ground surface, in the wells W1.1, 3, 5, 6, 8 and 9 (in red in Figure 1).

All the field samples were stored in 40 ml glass vials without headspace and sealed with Teflon lined screw caps. Biological activity in samples was prevented by adding ascorbic acid and by storing in darkness at 4°C until isotopic analysis (Verhack et al., in prep.).

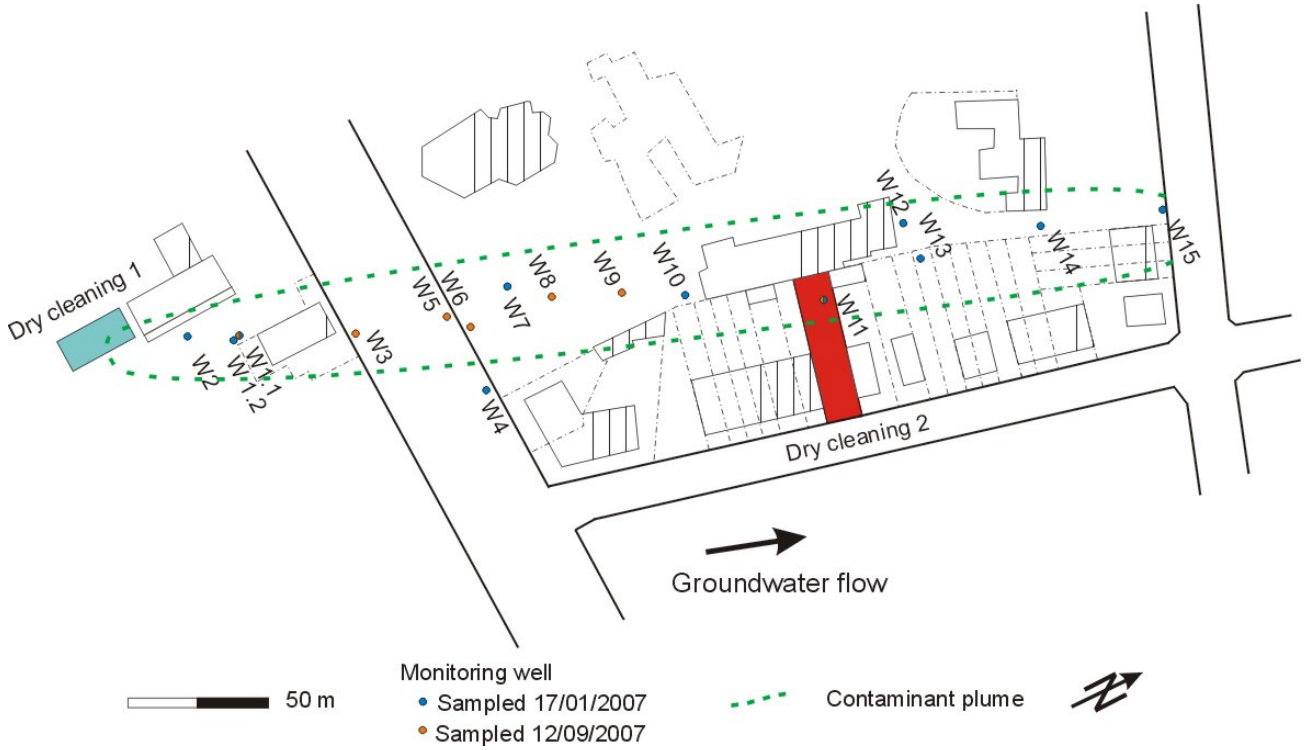

Figure 1: Schematic description of the investigated site located in Borsbeek with the location of the monitoring wells where the groundwater samples were sampled in two successive campaigns.

2.2. Experimental samples

Eleven experimental groundwater samples were selected inside the two experimental batches (Table 1) for the $\delta^{13}C$ measurements on VOCs done at IRMM.

The two experimental batches were conducted in 160 ml serum bottles using 30 g wet weight homogenized soil material and 100 ml of groundwater. Both soil and groundwater materials were sampled in the investigated site, away from the polluted areas. The used soil was sampled near the first dry cleaning at a depth of 3 to 7 m-bgs and the groundwater was selected in the well W4 (Figure 1). Inside each of the serum bottles containing the mixture of non-contaminated soil and groundwater, 10 to 15 µmol of PCE (99.99% purity, Sigma Aldrich) was added through the Viton® septa. The experiments were conducted during 78 days at 20°C in darkness without shaking. The aim and the set-up description of these experiments and summarized in the Table 1.

Table 1: Aim and set-up of the two experimental batches

Experiments	Aim	Set-up
1: R1A	Monitor the evolution of the concentrations and the $\delta^{13}C_{VPDB}$ of PCE, TCE and cDCE during abiotic degradation	Addition of formaldehyde and $HgCl_2$ solutions to prevent microbial activity
2: R4A	Monitor the biotic reductive PCE dechlorination stimulated by the addition of a carbon source	Addition of a sodium lactate solution to reach a final concentration of 200 mg C l^{-1} in the batch

The eleven experimental samples selected for this study are:

- Five groundwater samples, named : R1A-T4, -T5, -T7, -T8, -T9, taken in the abiotic batch (number 1 in Table 1) after 1, 6, 15, 54 and 78 days of experiments.
- The last six: R4A-T4, -T5, -T6, -T7, -T8, -T9 were selected in the biotic batch (i.e. biotic PCE dechlorination experiments stimulated by addition of sodium lactate, number 2 in Table 1) at 1, 6, 11, 15, 54 and 78 days.

All the preparative and sampling steps were performed in an anaerobic glove box in order to keep anaerobic conditions inside the bottles. After sampling, the experimental groundwater samples were stored in 8 ml vials filled without headspace, and acidified using 180 µl phosphoric acid with p_H<2. They were stored at 4°C before isotopic analysis.

3. Compound Specific Isotope Analysis

3.1. Headspace SPME extraction

The analysed VOCs (Volatile Organic Compounds) were extracted from the headspace above the aqueous samples using a 75 µm Carboxen-PDMS Solid Phase Micro-extraction (SPME) fibre (Supelco).

To reach a high accuracy and precision of the measurements, the groundwater samples were diluted up to 10 times in mineral water (used to mimic natural groundwater and optimize SPME extraction) in order to reach compounds concentrations lower than 1 µg. ml^{-1}. The diluted samples were put in 40 ml glass vials sealed with septa screw caps with around 30% (wt./vol.) of NaCl and about 25% headspace volume.

The SPME fibre was exposed to the headspace for 10 min while the aqueous sample was immersed in an ultrasonic bath. The fibre was desorbed into the hot GC inlet set at 240˚C for 1 min.

3.2. GC/C-IRMS

The $\delta_{VPDB}{}^{13}C$ were measured on PCE, TCE, cDCE, tDCE and in few cases of benzene, toluene, ethylbenzene, *m+p-, o*-xylene, extracted from the groundwater samples, at IRMM using a Trace gas chromatograph (Thermo) connected to a Delta*Plus* XP isotope ratio mass spectrometer (Thermo) via a combustion interface.

The GC was equipped with a DB-624 capillary column (60 m × 0.25 mm i.d., J&W Scientific Inc.) for the compounds separation. The carrier gas (He) flow rate was set at 2 ml min^{-1}. The oven temperature was programmed from 35 to 150°C at 2°C min^{-1} and from 150 to 240°C at 10°C min^{-1} with final hold time of 3 min. The temperature of the combustion reactor (CuO/NiO/Pt) was set at 940°C.

Two gas pulses of in-house reference CO_2 gas (pre-calibrated for its $\delta_{VPDB}{}^{13}C$ by EA-IRMS, Woulé Ebongué et al., 2009a) were introduced via the dedicated interface into the IRMS source to serve as a reference for the $\delta_{VPDB}{}^{13}C$ determined for the chromatographically separated compounds.

As the used reference is a gas, a mix of internal BTEX standards treated and analysed similarly to the samples was used as additional tool to check the accuracy of the hSPME - GC/C-IRMS system during routine analysis (Woulé Ebongué et al., 2009a). This mix of BTEX standards was then regularly analysed prior to the samples.

3.3. $\delta^{13}C$ and combined uncertainties calculations

The $\delta^{13}C$ of the targeted compounds expressed versus VPDB reference material (i.e. $\delta_{cpd, VPDB}{}^{13}C$) were calculated as following:

$$\delta_{cpd,\ VPDB}{}^{13}C = \delta_{cpd,\ CO2}{}^{13}C + \delta_{CO2,\ VPDB}{}^{13}C + (\delta_{cpd,\ CO2}{}^{13}C \times \delta_{CO2,\ VPDB}{}^{13}C / 1000)$$

$\delta_{cpd,\ CO2}{}^{13}C$ was calculated using ISODAT NT 2.0 software setting the CO_2 gas as the reference

The $\delta_{CO2,\ VPDB}{}^{13}C$ was previously calibrated and normalised using NBS19 and LSVEC references respectively, on the basis of EA-IRMS measurements (Woulé Ebongué et al., 2009a).

A first calibration of the CO_2 in-house reference gas was done in 2007, with a $\delta_{CO2,\ VPDB}{}^{13}C$ value of -13.94 ± 0.09‰ (std U) used for calculating the $\delta_{cpd,\ VPDB}{}^{13}C$ of the first analysed samples: i.e. the first 15 field samples taken in January 2007 and the 11 experimental samples. A second calibration of the same CO_2 gas was done beginning of 2008 prior to the analysis of the last set of the field samples. For these latter, the $\delta_{CO2,\ VPDB}{}^{13}C$ value of -13.81 ± 0.13‰ (std U) was used.

The two $\delta_{CO2,\ VPDB}{}^{13}C$ values were calculated using GUMWB software as following:

$$\delta_{CO2,\ VPDB}{}^{13}C = \delta_{CO2,\ NBS19}{}^{13}C + \delta_{NBS19,\ VPDB}{}^{13}C + (\delta_{CO2,\ NBS19}{}^{13}C \times \delta_{NBS19,\ VPDB}{}^{13}C / 1000)$$

$$\delta_{CO2,\ NBS19}{}^{13}C = \delta_{CO2,\ NBS19}{}^{13}C^* \times CF$$

Where $\delta_{CO2,\ NBS19}{}^{13}C^*$ is the measured $\delta_{CO2,\ NBS19}{}^{13}C$

The correction factor $CF = \delta_{LSVEC,\ NBS19}{}^{13}C / \delta_{LSVEC,\ NBS19}{}^{13}C^*$

Where $\delta_{LSVEC,\ NBS19}{}^{13}C^*$ is the measured $\delta_{LSVEC,\ NBS19}{}^{13}C$

By definition, $\delta_{NBS19,\ VPDB}{}^{13}C$ = +1.95‰ and $\delta_{LSVEC,\ NBS19}{}^{13}C$ = -48.4555‰, calculated from $\delta_{LSVEC,\ VPDB}{}^{13}C$ (= -46.6‰) (Coplen et al., 2006).

For all the calculated $\delta_{cpd,\ VPDB}{}^{13}C$, the uncertainties were calculated using GUMWB software by combining 1) the standard uncertainty from the $\delta_{CO2,\ VPDB}{}^{13}C$ measurements (in-house reference gas) by EA-IRMS and 2) the standard uncertainty from at least duplicated analysis of the compounds from the groundwater samples by GC/C-IRMS (with k = 2).

4. Results

4.1. Field samples

The resulting $\delta_{VPDB}{}^{13}C$ (‰) and their combined uncertainties (U) on tDCE, cDCE, TCE, PCE and if present on benzene, toluene, ethylbenzene, *m+p*-xylene and *o*-xylene from the 25 groundwater samples taken in the contaminant plume in the site of Borsbeek are noted in the following Table 2.

IRMM Registration number	Samples	Compounds	$\delta_{VPDB}{}^{13}C$ (‰)	Combined U
First sampling campaign: January 2007				
IM GAS-2007-02-002062	**1806.1 3-4**	TCE	-38.80	2.30
		PCE	-28.40	1.40
IM GAS-2007-02-002063	**2105.2 6-7**	TCE	-36.19	0.41
		PCE	-26.40	0.89
IM GAS-2007-02-002064	**307 3-4**	DCE	-18.62	0.92
		TCE	-22.66	0.18
		PCE	-26.04	0.28
IM GAS-2007-02-002065	**1301.1 10-13**	DCE	-26.70	0.50
IM GAS-2007-02-002067	**1807-1 6-7**	TCE	-41.80	2.30
		PCE	-20.05	0.60
IM GAS-2007-02-002069	**1806.2 6-7**	TCE	-36.10	1.20
		PCE	-23.43	0.37
IM GAS-2007-02-002070	**1204.1 10-11**	DCE	-25.37	0.57
		TCE	-22.76	0.37
		PCE	-23.50	1.10
IM GAS-2007-02-002071	**1301.3 6-7**	DCE	-40.10	1.90
		TCE	-32.40	1.40
		PCE	-23.69	0.58

IM GAS-2007-02-002072	**2102.2 6-7**	TCE	-27.35	0.59
		PCE	-15.57	0.20
IM GAS-2007-02-002073	**312 6-7**	PCE	-15.29	0.73
IM GAS-2007-02-002074	**1804.2 6-7**	TCE	-33.81	*nd*
		PCE	-23.90	1.90
IM GAS-2007-02-002075	**1801 11-12**	DCE	-39.50	1.90
		TCE	-41.90	1.80
		PCE	-21.56	0.62
IM GAS-2007-02-002076	**1301.2 8.5-9.5**	DCE	-30.83	0.51
		TCE	-17.63	0.23
		PCE	-8.21	0.24
		Benzene	-25.94	0.21
IM GAS-2007-02-002078	**2105.1 3-4**	PCE	-25.05	0.49
		TCE	-37.58	*nd*
		PCE	-24.00	*nd*
IM GAS-2007-02-002066	**WP**	*nd*	-	-
IM GAS-2007-02-002068	**2108-1 11-12**	TCE	-37.58	*nd*
		PCE	-24.00	*nd*
IM GAS-2007-02-002077	**1804.1 3-4**	*nd*	-	-
Second sampling campaign: September 2007				
IM GAS-2007-12-003050	**1109**	cDCE	-26.26	0.35
		TCE	-18.21	0.30
		PCE	-18.84	0.29
IM GAS-2007-12-003051	**1101**	tDCE	-30.00	0.37
		cDCE	-26.93	0.26
		TCE	-19.84	0.21
		PCE	-17.10	0.34
IM GAS-2007-12-003054	**SP2, 3-4**	tDCE	-28.37	0.16
		cDCE	-32.51	0.24
		TCE	-26.07	0.21
		PCE	-25.43	0.68
IM GAS-2007-12-003056	**SP1, 3-4**	cDCE	-27.94	0.28
		TCE	-40.53	0.08
		PCE	-22.85	0.89
IM GAS-2007-12-003057	**SP2, 5-6**	cDCE	-35.12	0.28
		TCE	-20.10	0.13
		PCE	-21.41	0.30
IM GAS-2007-12-003058	**SP1, 5-6**	tDCE	-29.00	1.10
		cDCE	-27.89	0.68
		TCE	-11.19	0.18
		PCE	-17.55	0.21
IM GAS-2007-12-003060	**1103**	cDCE	-26.49	0.08
		TCE	-22.90	0.32
		PCE	-23.72	0.09
IM GAS-2008-01-003053	**M3.1**	tDCE	-30.27	0.47
		cDCE	-29.96	0.15
		TCE	-18.13	0.09
		PCE	-18.45	0.19
IM GAS-2007-12-003055	**P1**	PCE	-25.52	0.75
IM GAS-2007-12-003052	**307**	tDCE	-27.98	0.13
		cDCE	-20.59	0.56
		TCE	-22.89	0.90
		PCE	-23.09	0.29

		tDCE	-29.16	0.28
		cDCE	-22.06	0.69
		TCE	-25.70	0.72
		PCE	-23.49	0.28
IM GAS-2007-12-003059	**407**	Benzene	-29.31	0.14
		Toluene	-22.84	0.33
		Ethylbenzene	-26.94	0.31
		m+p-xylene	-26.50	0.64
		o-xylene	-20.66	0.96

4.2 Experimental samples

Table 3 shows the resulting $\delta_{VPDB}{}^{13}C$ (‰) and the combined uncertainties (U) measured on PCE, TCE, cDCE and if present benzene and ethylbenzene compounds from the 11 experimental samples in the two experimental batches R1 A and R4 A.

IRMM Registration number	Samples	Compounds	$\delta_{VPDB}{}^{13}C$ (‰)	Combined U
IM GAS-2007-03-002179	**R1 A T4**	PCE	-28.63	0.81
IM GAS-2007-03-002186	**R1 A T5**	TCE	-48.89	*nd*
		PCE	-35.20	1.20
IM GAS-2007-03-002183	**R1 A T7**	PCE	-35.00	2.00
IM GAS-2007-03-002184	**R1 A T8**	PCE	-32.80	1.20
IM GAS-2007-03-002187	**R1 A T9**	*nd*	-	-
IM GAS-2007-03-002178	**R4 A T4**	*nd*	-	-
IM GAS-2007-03-002180	**R4 A T5**	TCE	-29.50	*nd*
		PCE	-36.01	0.58
		Benzene	-24.32	0.33
		Ethylbenzene	-25.40	0.84
IM GAS-2007-03-002181	**R4 A T6**	TCE	-30.48	0.72
		PCE	-34.67	0.96
		Benzene	-24.15	0.18
		Ethylbenzene	-25.16	0.19
IM GAS-2007-03-002182	**R4 A T7**	TCE	-30.30	1.10
		PCE	-33.10	1.90
		Benzene	-24.05	0.26
		Ethylbenzene	-25.55	0.76
IM GAS-2007-03-002185	**R4 A T8**	*c*DCE	-49.14	0.41
		TCE	-33.81	0.55
		PCE	-23.60	1.30
		Benzene	-24.48	0.30
		Ethylbenzene	-25.53	0.37
IM GAS-2007-03-002188	**R4 A T9**	*c*DCE	-52.44	0.66
		TCE	-21.20	1.10
		Benzene	-24.32	0.30
		Ethylbenzene	-25.80	1.10

5. Conclusions

The Compound Specific Isotope Analysis (CSIA) methods already developed at IRMM for carbon isotopic ratio measurements on VOCs from soil and groundwater (Woulé Ebongué et al., 2009 b) were again successfully applied to groundwater samples from the industrial site of Borsbeek.

This work demonstrated the capability of IRMM's equipment and staff to respond external customers demand such as VITO and to provide accurate $\delta_{VPDB}{}^{13}C$ (‰) results with reliable uncertainties estimation calculated as budgets using GUMworkbench software.

This work also provides evidence for the potential application of CSIA to two inter-dependent issues in field studies which are sources fingerprinting/ apportionment and monitoring in situ VOCs degradation.

The scientific interpretation of these isotopic data measured on VOCs from both natural and experimental samples, together with the compounds concentrations measured at VITO by GC-MS, is detailed in the Chapter 5 of the Ph. D. thesis manuscript of Jeroen Verhack (Verhack et al., in prep). This Ph. D. work is evaluating CSIA as a tool to allocate contaminant plumes to their respective sources and then to identify the contribution of the different sources to the observed aquifer contamination for this specific industrial site. CSIA is also investigated in vitro in order to provide a semi-quantitative evaluation of the in situ biodegradation on the carbon isotopic compositions of the target compounds.

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European Commission

EUR 23689 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: Report on the $\delta_{VPDB}{}^{13}C$ measurements on Volatile Organic Compounds from groundwater samples using Compound Specific Isotope Analysis.
Authors: V. Woulé Ebongué, B. Geypens, M. Berglund
Luxembourg: Office for Official Publications of the European Communities
2008 – 10 pp. – 21.0 x 29.7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN 978-92-79-11164-8
DOI 10.2787/17830

Abstract
The report shows that the Compound Specific Isotope Analysis (CSIA) methods for carbon were successfully applied to the analysis of Volatile Organic Chlorinated compounds (VO-Cl) from groundwater samples selected in an industrial site is seated in Borsbeek (Belgium). Former soil and groundwater investigations in this site indicated the presence of underground contamination by VO-Cl. This contamination was likely linked to the activities of two former dry cleaning facilities.
This report describes the material, the techniques and the methods used for measuring the $\delta_{VPDB}{}^{13}C$ of the VO-Cl in the 25 groundwater samples from the industrial site of Borsbeek and that of 11 samples from experimental batches. This report also demonstrated the capability of IRMM's equipment and staff to respond external customers demand such as VITO and to provide accurate $\delta_{VPDB}{}^{13}C$ (‰) results with reliable uncertainties estimation calculated as budgets using GUMworkbench software.
This work also provides evidence for the potential application of CSIA to two inter-dependent issues in field studies which are sources fingerprinting/ apportionment and monitoring in situ VOCs (Volatile Organic Compounds) degradation.

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LA-NA-23689-EN-C

ISBN 978-92-79-11164-8

Publications Office
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